# **Section 2.0** Characteristics of Coal Mine Drainage Discharges

Acid mine drainage is generated when sulfide minerals, principally pyrite (FeS<sub>2</sub>), are exposed to increased amounts of air and water in the oxidizing and non-alkaline environment of a surface or underground mine. The sulfide minerals typically occur in coal beds as well as in strata overlying and underlying the coal. Weathering and aqueous dissolution of the sulfide mineral oxidation products, including dissociated sulfuric acid and metals (e.g., Fe, Mn, Al), produces surface and groundwater degradation. Explanations of the chemical reactions by which acid mine drainage is produced from pyrite and other iron sulfide minerals are found in Singer and Stumm (1970), Kleinmann et al. (1981), Lovell (1983), Evangelou (1995), and Rose and Cravotta (1998). Additional references presenting data and discussion of factors related to pyrite oxidation rates include Emrich (1996), McKibben and Barnes (1986), Moses and Herman (1991), Watzlaf (1992), and Rimstidt and Newcomb (1993). These reactions also are presented and discussed in Section 2.0 of EPA's Coal Remining Best Management Practices Guidance Manual.

While pyrite is the most commonly reported producer of AMD, other mineral species including the sulfide mineral marcasite (FeS<sub>2</sub>), and sulfate minerals jarosite (KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) and alunite (KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>), are capable of producing acidic drainage at surface and underground mine sites. Sulfate minerals are generally secondary weathering products of pyrite oxidation. Nordstrom (1982) shows the sequence by which these minerals can form from pyrite. Many secondary sulfate minerals have been identified that are typically very soluble and transient in the humid eastern United States. These minerals form during dry periods and are flushed into the ground-water system during precipitation events. The sulfate minerals that contain iron, aluminum, or manganese are essentially stored acidity and will produce acid when dissolved in water. Sulfate minerals such as melanterite, pickeringite, and halotrichite occur commonly in Appalachian Basin coal-bearing rocks. Additional information about these sulfate minerals is found in Cravotta (1994), Lovell (1983), Rose and Cravotta (1998), and Brady et al. (1998).

Acid mine drainage is the most frequently described and most environmentally damaging type of coal mine drainage. However, other damaging types can occur due, principally, to geologic factors and influences from mining and reclamation practices. According to Rose and Cravotta (1998):

"Coal Mine drainage ranges widely in composition, from acidic to alkaline, typically with elevated concentrations of sulfate (SO<sub>4</sub>), iron (Fe), manganese (Mn), and aluminum (Al) as well as common elements such as calcium, sodium, potassium, and magnesium. The pH is most commonly either in the ranges 3 to 4.5 or 6 to 7, with fewer intermediate or extreme values... Acidic mine drainage (AMD) is formed by the oxidation of pyrite to release dissolved Fe<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup>, followed by the further oxidation of the Fe<sup>2+</sup> to Fe<sup>3+</sup> and the precipitation of the iron as a hydroxide ("yellow boy") or similar substance, producing more H<sup>+</sup>...In contrast, neutral or alkaline mine drainage (NAMD) has alkalinity that equals or exceeds acidity but can still have elevated concentrations of SO<sub>4</sub>, Fe, Mn and other solutes. NAMD can originate as AMD that has been neutralized by reaction with carbonate minerals, such as calcite and dolomite, or can form from rock that contains little pyrite. Dissolution of carbonate minerals produces alkalinity, which promotes the removal of Fe, Al and other metal ions from solution, and neutralizes acidity. However, neutralization of AMD does not usually affect concentrations of SO<sub>4</sub>."

The rate of AMD production and the concentrations of acidity, sulfate, iron, and other water quality parameters in mine drainage are dependent upon numerous physical, chemical, and biological factors. According to Rose and Cravotta (1998):

"Many factors control the rate and extent of AMD formation in surface coal mines. More abundant pyrite in the overburden tends to increase the acidity of drainage, as does decreasing grain size of the pyrite. Iron-oxidizing bacteria and low pH values speed up the acid-forming reaction. Rates of acid formation tend to be slower if limestone or other neutralizers are present. Access of air containing the oxygen needed for pyrite oxidation is commonly the limiting factor in rate of acid generation. Both access of air and exposure of pyrite surfaces are promoted by breaking the pyrite-bearing rock. The oxygen can gain access either by molecular diffusion through the air-filled pore space in the spoil, or by flow of air which is driven through the pore space by temperature or pressure gradients..."

Numerous studies have evaluated the distribution of total sulfur contents and pyritic sulfur contents within coals and overburden strata. In some of these studies, investigations have examined the significance of pyrite morphology, especially the framboidal form with high surface area.

AMD discharges in Pennsylvania range in flow from seeps of less than 1 gallon per minute (gpm) to abandoned underground mine outfalls such as the Jeddo Tunnel near Hazleton, PA where a flow greater than 150,000 gpm (40,000 gpm average flow) has been measured. Table 2.0a presents typical and extreme examples of acidity, alkalinity, and related water quality parameters in coal mine drainage (from surface mines, underground mines, and coal refuse piles) and nearby well and spring samples. These water samples were compiled from data in Hornberger and Brady (1998) and Brady et al. (1998) to illustrate mine drainage quality variations in Pennsylvania. Similar variations in mine drainage quality exist in West Virginia, Ohio, and other states in the Appalachian Basin. Acidity and alkalinity concentrations greater than 100 mg/L are shown in bold in Table 2.0a.

Some of the most extreme concentrations of acidity, iron, and sulfate in Pennsylvania coal mine drainage, have been found at the Leechburg Mine refuse site in Armstrong County, and at surface mine sites in Centre, Clinton, Clarion, and Fayette Counties (Table 2.0a). Acidity concentrations of seeps from Lower Kittanning Coal refuse at the Leechburg site exceed 16,000 mg/L, while the sulfate concentration of one sample exceeds 18,000 mg/L. Schueck et al. (1996) reported on AMD abatement studies conducted at a backfilled surface mine site in Clinton County. A monitoring well that penetrated a pod of buried coal refuse produced a maximum acidity concentration of 23,900 mg/L prior to the implementation of the abatement measures.

 Table 2.0a:
 High Alkalinity Examples in Pennsylvania Mine Discharges

Site Name	Stratigraphic Interval	pН	Alkalinity mg/L	Acidity mg/L	Fe mg/L	Mn mg/L	SO <sub>4</sub> mg/L	Flow gpm	Comments
Willow Tree	Waynesburg	7.8	379.0	0.0	0.12	0.04	165.0	1.0	Seep at deep mine, pre-mining
Susan Ann	Waynesburg	3.3	0.0	1500.0	324.40	89.70	2616.0	< 1.0	Seep near sealed deep mine entry
Bertovich	Sewickley	3.1	0.0	378.0	74.80	9.14	1098.0	2.0	Deep mine discharge
Smith	Redstone	7.7	246.0	0.0	1.47	0.27	122.0	0.0	Pit water at lowwall sump
Brown	Redstone	7.4	626.0	0.0	1.65	1.05	1440.0	no data	Spring near cropline
Trees Mills	Pittsburgh	2.5	0.0	3616.0	190.40	13.50	1497.8	13.0	Deep mine discharge
State Line	Upper & Lower Bakerstown	8.1	210.0	0.0	< 0.30	1.37	416.0	no data	Post-mining seep from backfilled spoil
Cover Hill	Lower Bakerstown	3.6	0.0	168.1	0.83	14.60	787.0	1.8	Discharge from abandoned pit below site
Hager	Brush Creek	6.8	189.4	no data	0.21	0.40	68.2	4.0	Logan spring
Fruithill	Upper & Lower Freeport	7.8	238.0	0.0	0.01	0.01	458.0	60.0	Deep mine discharge
Laurel Hill #1	U. Freept. to U. Kittng.	8.1	484.0	0.0	0.97	1.98	590.0	no data	Toe of spoil seep
Morrison	Upper Kittanning	7.0	308.0	0.0	0.63	3.49	327.0	< 1.0	Seep near collection ditch
Stuart	Upper Kittanning	2.8	0.0	1290.0	56.70	49.20	1467.0	no data	Seep, sandstone overburden
Clinger	Middle Kittanning	6.8	190.0	0.0	< 0.30	1.28	184.0	0.0	Pit water
Leechburg	Lower Kittanning	2.4	0.0	16718.0	> 300.0	19.30	18328.0	2.0	Seep from coal refuse disposal area
* Fran	Lower Kittanning	2.2	0.0	23900.0	5690.00	79.00	25110.0	0.0	Monitoring well in backfilled spoil
Swiscambria	Lower Kittanning	4.2	5.0	88.0	0.09	24.20	1070.0	no data	Seep, freshwater paleoenvironment
Albert #1	Lower Kittanning	3.1	0.0	1335.0	186.00	111.00	3288.0	55.0	Spoil discharge, brackish paleoenviron.
Snyder #1	Lower Kittanning	6.9	114.0	0.0	1.10	3.14	264.0	0.0	Pit water, marine paleoenvironment
Lawrence	Lower Kittanning	2.2	0.0	5938.0	2060.00	73.00	3600.0	0.0	Pit water, sandstone overburden
Graff Mine	L. Kittng. & Vanport Ls	7.8	274.0	no data	0.01	1.13	1645.0	10.0	Seep above road
Philipsburg	Clarion	2.7	0.0	9732.0	1959.80	205.30	4698.0	35.0	Spoil discharge
** Old 40	Clarion	2.2	0.0	10000.0	3200.00	260.00	14000.0	0.0	Monitoring well in backfilled spoil
Orcutt	Clarion	3.9	0.0	5179.6	2848.00	349.00	11120.0	0.0	Spoil water from piezometer

Site Name	Stratigraphic Interval	pН	Alkalinity mg/L	Acidity mg/L	Fe mg/L	Mn mg/L	SO <sub>4</sub> mg/L	Flow gpm	Comments
Cousins	Clarion	7.6	130.0	0.0	7.15	0.30	71.0	0.0	Pit water, glacial till influence
Zacherl	Clarion	2.3	0.0	9870.0	2860.00	136.60	7600.0	no data	Toe of spoil discharge
Horseshoe	Mercer	2.3	0.0	1835.0	194.00	27.00	2510.0	700.0	Abandoned deep mine discharge
Wadesville	Llewellyn	6.7	414.0	0.0	3.61	3.37	1038.0	no data	Minepool, Anthracite Region

Note: Extreme values (>100 mg/L) of alkalinity and acidity are highlighted for emphasis

Since the alkalinity-production process has a dramatically different set of controls, the resultant maximum alkalinity concentrations found in mine environments are typically one or two orders of magnitude less than the maximum acidity concentrations. Examples of relatively high alkalinity concentration in mine drainage, ground water, and surface water associated with Pennsylvania bituminous and anthracite coal mines are presented in Table 2.0a. The highest natural alkalinity concentration found in PA DEP mining permit file data (and reported in Table 2.0a) is 626 mg/L in a spring located near the cropline of the Redstone Coal in Fayette County. Thick sequences of carbonate strata, including the Redstone Limestone and the Fishpot Limestone underlie and overlie the Redstone Coal.

Carbonate minerals (e.g., calcite and dolomite) play an extremely important role in determining post-mining water chemistry. They neutralize acidic water created by pyrite oxidation, and there is evidence that they also inhibit pyrite oxidation (Hornberger et al., 1981; Williams et al., 1982; Perry and Brady, 1995). Brady et al. (1994) concluded that the presence of as little as 1 to 3 percent carbonate (on a mass-weighted basis) at a mine site can determine whether that mine produces alkaline or acid water. Although pyrite is clearly necessary to form acid mine drainage, the relationship between the amount of pyrite present and water-quality parameters (e.g., acidity) was only evident where carbonates were absent (Brady et al., 1994).

The paleoclimatic and paleoenvironmental influences on rock chemistry in the northern Appalachians resulted in the formation of coal overburden with greatly variable sulfur content (0 percent to >15 percent S) and calcareous mineral content (0 percent to >90 percent CaCO<sub>3</sub>) as

<sup>\*</sup> data from Schuek et al. (1996)

<sup>\*\*</sup> data from Dugas et al. (1993)

shown on figures of overburden drill hole data in Brady et al. (1998). The wide variations in rock chemistry contribute to the wide variations in water quality associated with surface coal mines. Figures 2.0a and 2.0b show the frequency distributions (i.e., range) of pH in mine discharges in the bituminous and anthracite coal regions of Pennsylvania. The origin and significance of this bimodal frequency distribution for mine drainage discharges are described in Brady et al. (1997, 1998) and Rose and Cravotta (1998). Brady et al. (1997) explained that although pyrite and carbonate minerals only comprise a few percent (or less) of the rock associated with coal, these acid-forming and acid-neutralizing minerals, respectively, are highly reactive and are mainly responsible for the bimodal distribution. Depending on the relative abundance of carbonates and pyrite, and the relative weathering rates, the pH will be driven toward one mode or the other.

Variations in the chemical composition of mine drainage discharges are principally related to geologic and hydrologic factors. The hydrologic factors that cause individual mine drainage discharges to vary in flow and concentrations of acidity, alkalinity, sulfates and metals (e.g., Fe, Mn, Al) throughout the water year are discussed in the following sections of this chapter.

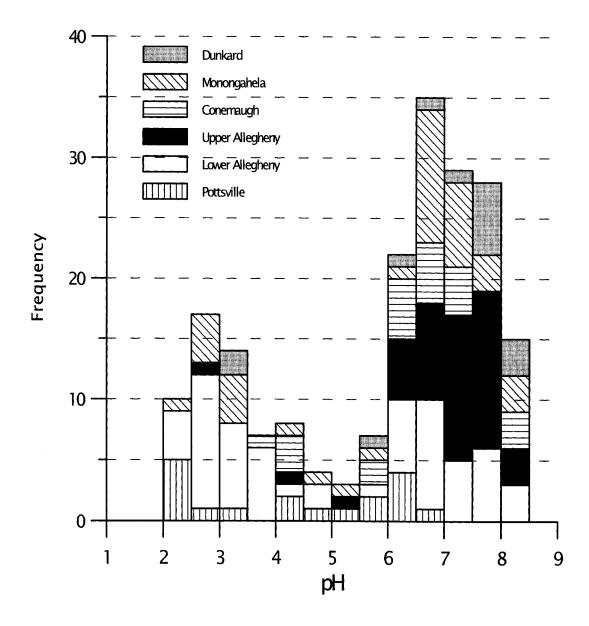


Figure 2.0a: Distribution of pH in Bituminous Mine Drainage

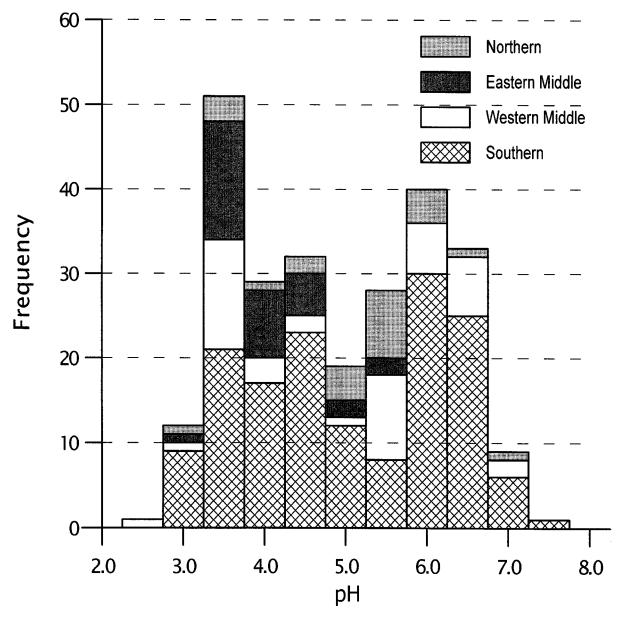


Figure 2.0b: Distribution of pH in Anthracite Mine Drainage

### 2.1 Impact of Stream Flow Variation on Water Quality Parameters

Annual variations in streamflow and surface water quality degraded by AMD discharges can be very significant as shown in Hornberger et al. (1981) for water quality network stations including small streams and large rivers in western Pennsylvania. These water quality network stations are closely monitored by PADEP. The streams are sampled several times yearly and analyzed for a wide array of water quality parameters, and usually are located in close proximity to U.S. Geological Survey (USGS) stream hydrograph stations for which extensive streamflow data area compiled and published. The data from the network stations is contained in the STORET database maintained by EPA.

The water quality network station with the greatest range in streamflow and concentration of AMD related water quality parameters is the Dunkard Creek Station, in Greene County, Pennsylvania (Hornberger et al., 1981). This compilation includes greater than 150,000 lines of STORET data. Streamflow varied between 2 cubic feet per second (cfs) and 4,020 cfs in approximately 100 samples collected between 1950 and 1976, while the concentration of sulfates ranged from 40 to 4000 mg/L. The annual cycles of streamflow variations from October 1960 to September 1970 for Dunkard Creek are shown in Figure 2.1a, which was plotted by Hornberger et al. (1981) from monthly means of discharge data compiled by the U.S. Geological Survey.

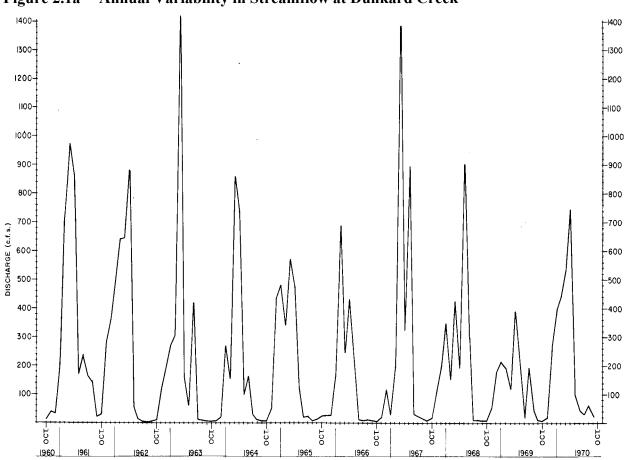
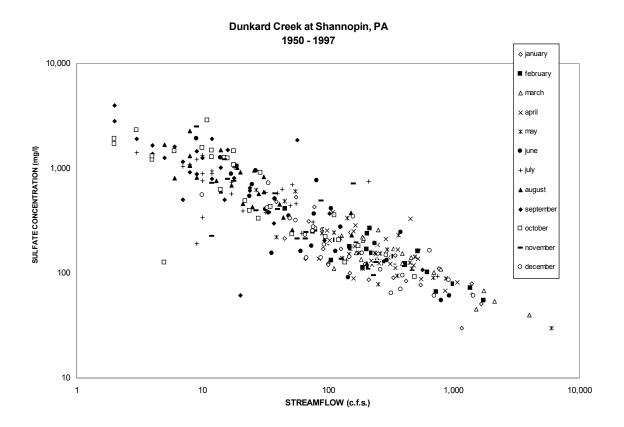


Figure 2.1a Annual Variability in Streamflow at Dunkard Creek

In order to examine the relationship between variations in streamflow and corresponding variations in a reliable water quality indicator parameter, a logarithmic plot of sulfate concentration versus discharge was constructed using procedures described in Gunnerson (1967), Hem (1970), and Hornberger et al. (1981). The sulfate concentrations in Dunkard Creek tend to systematically decrease with increasing flow as shown by the approximately linear inverse relationship on Figure 2.1b. However, the relationship between streamflow and concentration may be more appropriately defined by a general elliptical progression of monthly flow and water quality relationships surrounding a least squares line fitted to the data points, similar to that found by Gunnerson (1967) and Hornberger et al. (1981). The tendency for high flow accompanied by low sulfate concentration in January, February, March, April, and May and low flow accompanied by high sulfate concentration in July, August, September, and October, and other flow-quality relationships throughout the water year may be observed in Figure 2.1b. Figure 2.1b includes almost 50 years of data (1950-1997) that show a stronger inverse linear relationship between sulfate concentration and streamflow than was shown in the first 26 years of data (Hornberger et al., 1981). The correlation coefficient (r) between sulfate concentration and streamflow data in Figure 2.1b is -0.887 (for logarithmically transformed data), which is statistically significant at the 1 percent level (N=307). The coefficient of determination [r<sup>2</sup>] for this dataset is 0.787; therefore, 78.7 percent of the variations in sulfate concentration of the Dunkard Creek are accounted for by variations in streamflow. Similar patterns of variation in sulfate concentration and flow of a major AMD-impacted river were found (Hornberger et al., 1981) for the West Branch Susquehanna River at Renovo, Pennsylvania.

Figure 2.1b: Sulfate Concentration vs. Streamflow at Dunkard Creek



### 2.2 AMD Discharge Types and Behaviors

Discharges of acid mine drainage (AMD) can exhibit very different behavior depending upon the type of mine involved and its geologic characteristics. The hydrologic characteristics of a pre-existing AMD discharge can have important ramifications for documenting baseline pollution load – affecting the frequency and duration of sampling required to obtain a representative baseline. Braley (1951) was among the first to study the hydrology of AMD discharges. He noted that, much like a stream, flow rates vary dramatically in response to precipitation events and seasons, and that acid-loading rates are chiefly a function of flow. The greater the flow, the greater the load. Smith (1988), looking at long-term records of AMD discharges in Pennsylvania, classified discharges based on three fundamental behaviors: 1) High flow - low concentration / low flow - high concentration response, where the flow rate varies inversely with concentration; 2) Steady response where changes in flow rate and chemistry are minimal or damped; and 3) "Slug" response where large increases in discharge volumes are not accompanied by corresponding reductions in concentrations, resulting in large increases in pollution loading.

Figure 2.2a presents the discharge and acidity hydrograph of a mine discharge exhibiting the first (high flow - low concentration / low flow - high concentration) behavior. This discharge drains from a relatively small underground mine complex (Duffield, G.M., 1985). Typical for this type of discharge, the flow rate varies greatly and is subject to seasonal flow variations as well as individual precipitation events. Acidity concentrations vary inversely with the discharge rate, with the highest acidity occurring during the low-flow months of September, October, and November. The inverse log-linear relationship between discharge and acidity is shown in Figure 2.2b. Acidity steadily decreases with increasing flow, reflecting dilution of the mine drainage during periods of abundant ground-water recharge. Nonetheless, the pollution loading (i.e., the total acidity produced from the discharge in pounds per day) increases during high-flow events, as the decrease in acidity is not commensurate with a given increase in flow. In this sense, the discharge behaves very much like a stream and is subject to large increases in flow which dilute the concentration of dissolved chemical constituents. However, concentration decreases are not

enough to offset flow increases. Pollution loading tends to parallel the flow rate but in a more subdued manner. The majority of pre-existing AMD discharges in Pennsylvania exhibit this type of behavior. It is most common for surface mine discharges and discharges from small to medium size underground mines where the capacity for ground water storage is relatively small and ground water flow paths are short.

Some discharges, particularly large-volume discharges from extensive underground mine complexes, show comparatively little fluctuation in discharge rate and only minor variation in chemical quality. Figure 2.2c presents such an example from a Schuylkill County, Pennsylvania, anthracite underground mine. In this case, the exceptionally large recharge area and volume of water in the mine pool, and the stratification of water quality within the mine pool, are causing a steady-response behavior of the discharge. Short-term fluctuations in flow and quality are subdued, because of the large amount of stored ground water acting as a reservoir and dampening fluctuations due to individual recharge events.

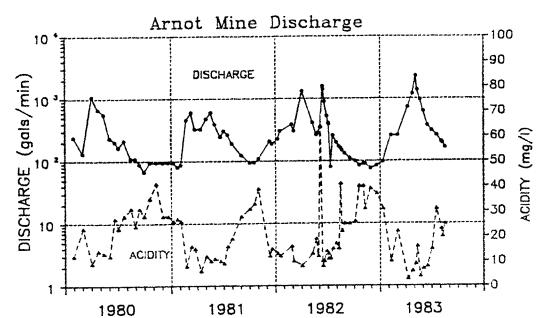


Figure 2.2a: Acidity and Streamflow of Arnot Mine Discharge

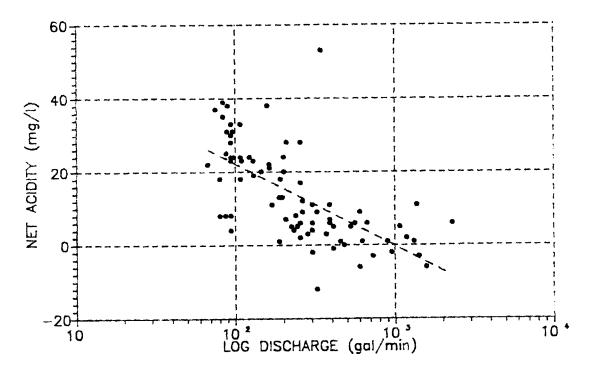


Figure 2.2b: Inverse Loglinear Relationship between Acidity and Streamflow

Occasionally, AMD discharges are subject to extreme variations in flow rates with little change in water quality. Figure 2.2d presents flow and acidity exhibiting "slug" behavior in a discharge from a coal refuse pile. Flow rates vary dramatically in response to recharge events (from less than 3 to 470 gpm). Concomitantly, acidity concentrations change very little and result in large, rapid variations in acid loading. This discharge behavior results where conditions favor the accumulation of water-soluble, acid-bearing shales in the unsaturated zone. During recharge events, infiltrating water permits rapid dissolution of salts producing additional acidity in the discharge, rather than causing a dilution effect. The longer the time period between recharge events, the more time is available for the build up of acid-bearing salts in the unsaturated zone. Coal refuse piles, and surface mines with very high sulfur spoil in the unsaturated zone and limited ground-water storage capacity, provide the most favorable environment for this discharge behavior. In the most severe cases, increases in flow can be accompanied by increased concentrations of acidity or metals, resulting in extreme increases in loading rates. When this

Figure 2.2c: Streamflow and Acidity in Schuylkill County

MARKSON AIRWAY - 1985

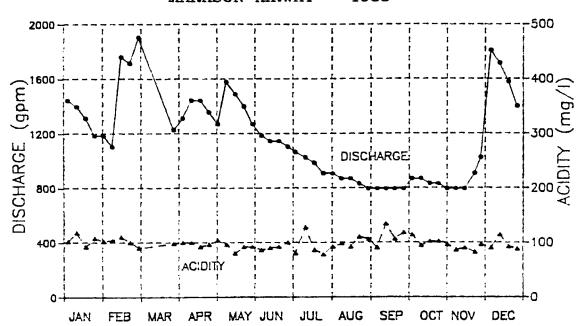
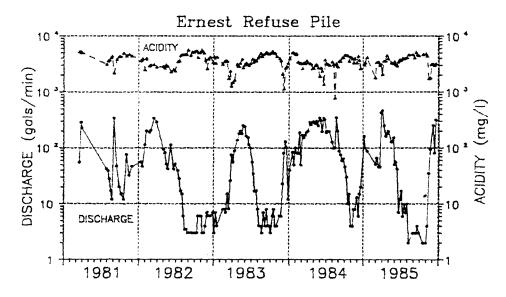


Figure 2.2d: Streamflow and Acidity in Coal Refuse Pile



phenomenon occurs on a large scale, potentially disastrous increases in acid loading can adversely affect downstream water uses and aquatic life.

The Arnot, Markson, and Ernest mine drainage discharges described in the preceding paragraphs were originally studied and graphically presented in Smith (1988) and Hornberger et al. (1990). These three mine drainage discharges are also the subject of three of the eight water quality reports completed by Griffiths (1987, 1988) as part of the cooperative EPA/PADEP remining project and included in the abridged volume by EPA (2001, EPA-821-B-01-014).

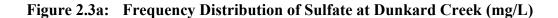
For remining operations that will reaffect a pre-existing pollutional discharge, knowledge of discharge behavior is critical to the establishment of a representative baseline. All three discharge types exhibit some seasonal behavior, with highest flows during seasonal high ground-water conditions and the lowest flows and loadings during low ground-water conditions. For most of Appalachia, high ground-water conditions occur during late winter or spring. Low ground-water conditions occur during late summer and early fall. The baseline sampling period must cover the full range of seasonal conditions. Exactly when these extremes will occur is unpredictable, as storm events may occur over relatively short time intervals. Accordingly, to properly characterize an AMD discharge, it is usually necessary to monitor the discharge over at least an entire water year with a sufficiently narrow sampling interval to capture short-term extreme events. Slug-response discharges may require more frequent sampling due to their flashy hydrologic response with large variations in pollution load over short time intervals. Conversely, less frequent baseline sampling may be adequate for damped-response discharges.

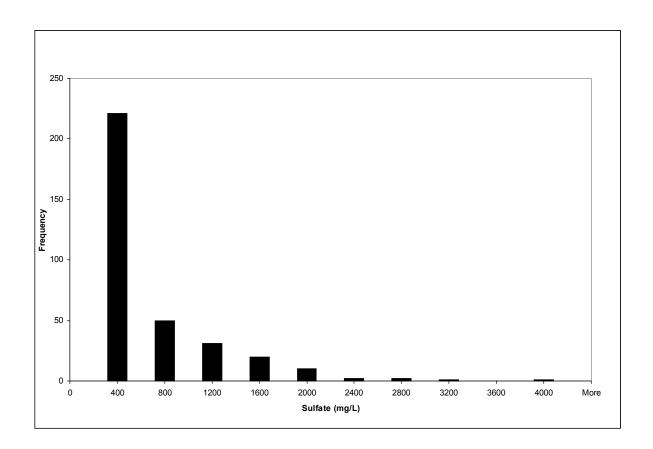
Because the baseline is based on loading rates, accurate flow measurements are as important as contaminant concentration measurements. Previous studies by Smith (1988), Hornberger et al. (1990), and Hawkins (1994) have emphasized the strong relationship between flow rate and contaminant load. Hawkins (1994) analyzed pre- and post-remining hydrologic data from 24 remining sites in Pennsylvania and noted that flow was the dominant factor in changes in post-mining pollution loads. Most remining operations that reduced baseline pollution load did so by reducing the flow of the pre-existing discharge. In view of this, Smith (1988) points out

that proper flow measurement is of overriding importance in determining the baseline pollution load.

## 2.3 Distributional Properties of AMD Discharges

Water quality parameters of many AMD discharges and AMD impacted streams are not normally distributed. In most cases these frequency distributions are highly skewed because there are many samples with relatively low concentrations and a few samples with very high concentrations due to low-flow drought conditions or slugs of pollution in response to major storm events. Plotting these data on a logarithmatic scale (as shown on Figure 2.1b), or logarithmically transforming the data produces a much closer approximation of the normal frequency distribution.





Numerous variables with continuous data on the interval or ratio level of information exhibit log normal behavior in the natural environment (Aitchison and Brown, 1973; Krumbein and Graybill, 1965; Griffiths, 1967), and logarithms are frequently used in the analysis and graphical expression of water quality data (Gunnerson, 1967; Hem, 1970). The log normal distribution is also very common in previous EPA work with wastewater discharges. Figure 2.3a shows the skewed frequency distribution for the sulfate data for the Dunkard Creek dataset used in Figure 2.1b.

Examples of the distributional properties of data from AMD discharges at remining sites in Pennsylvania are shown in Figures 2.3b to 2.3f from the EPA publication <u>Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollutant Load</u> (EPA-821-B-01-014), which is a companion volume to this report. The figures show frequency distributions of data using stemand-leaf diagrams. For additional information on stem-and-leaf diagrams, see Hoaglin et al. 1983.

Figure 2.3b shows a nearly normal frequency distribution of pH of the Arnot 003 discharge (N=82). An example of a highly skewed frequency distribution is given in Figure 2.3c for flow of the Clarion discharge. Following logarithmic transformation, the frequency distribution becomes more symmetrical, approaching normality, as seen in Figure 2.3d. However, some caution must be exercised in applying log transformations to data sets because overcorrection may occur. Such overcorrection is seen in the irregular frequency distribution of acidity concentration in the Clarion discharge. In Figure 2.3e, the untransformed data are somewhat positively skewed. Following transformation, these data become highly negatively skewed (Figure 2.3f).

Figure 2.3b: Stem-and-leaf Diagram of pH (Arnot 003)

N = 82		
Leaf Uni	t = 0.010	
1	30	4
2	30	7
5	31	134
17	31	555667888999
36	32	0011111112234444444
(15)	32	555666777789999
31	33	001111222234
19	33	556666778
10	34	1122
6	34	679
3	35	0
2	35	7
1	36	
1	36	
1	37	0

Figure 2.3c: Stem-and-leaf Diagram of Discharge

```
N = 77
Leaf Unit = 1.0
(53)
                 0000000001111222333333344444555555566666667788999999\\
24
         1
                 00222244444
13
         2
                 001288
7
         3
                 066
4
         4
                 0
3
         5
                 0
2
         6
2
         7
         8
2
                 3
         9
1
         10
1
         11
         12
         13
         14
1
         15
1
         16
1
         17
                 2
```

Figure 2.3d: Stem-and-leaf Diagram of Log Discharge

```
N = 75
Leaf Unit = 0.10
         -1
                3000
7
         -0
                766
         -0
11
                4330
19
         0
                01124444
(35)
         0
                55555666666777777777888888999999999\\
21
         1
                000111111333344
6
         1
                55679
         2
1
                2
```

Figure 2.3e: Stem-and-leaf Diagram of Acidity

N = 96						
Leaf Unit = 10						
8	0	00114568				
21	1	0234466667788				
30	2	033356899				
38	3	01245778				
(14)	4	01114456788899				
44	5	0112778899				
34	6	03344678				
26	7	014499				
20	8	15				
18	9	1455568899				
8	10	38				
6	11	09				
4	12	04				
2	13	8				
1	14					
1	15	4				

Figure 2.3f: Stem-and-leaf Diagram of Log Acidity

N= 97					
Leaf Unit = $0.10$					
1	-1	0			
1	-0				
2	-0	0			
3	0	3			
3	0				
5	1	22			
9	1	6679			
31	2	001112222222333444444			
(58)	2	55555556666666666666667777777777788888888			
8	3	0000011			

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